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A SUPERFICIAL SYNTHESIS OF SELENIUM NANOSPHERES USING WET CHEMICAL APPROACH

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ABSTRACT

Dextrin stabilized Selenium spherical nanoparticles have been successfully synthesized from a simple and a wet chemical approach by reducing sodium selenite, a selenium salt with Ascorbic Acid at room temperature in this study. The stirring effect and the effect of varied ratios were studied on controlling the nucleation of the nanoparticles (20-30nm) and reducing the polydispersity index. The nanoparticles were coated with dextrin maintaining the stability of the nanoparticles. The morphology and purity of the obtained nanoparticles were studied using various analytical tools.

KEYWORDS: Selenium, Nanoparticles, Dextrin, Ascorbic Acid, Sodium Selenite and Polydispersity Index

INTRODUCTION

Selenium is a metalloid from chalcogen family in the periodic table (group 16). It can exist in a range of oxidation states from +6 to -2 [1]. Selenium having a direct band gap of 1.7eV is a semiconductor with properties such as photoconductivity, photosensitivity and is used in xerography, rectifiers etc. Selenium is an essential micronutrient and can also play a major role in human body by enhancing the activity of the glutathione peroxidase and seleno-enzymes which in-turn can help in protecting the body from the free radicals which destroy the cells of the body causing autoimmune diseases. Selenium is commonly used as a nutritional supplement and the effects of selenium have been shown only after higher concentration of the selenium is added to the diet [2].

Over a decade nanoparticles have been used for many aspects and are defined as particulate dispersions or solid particles with a size in the range of 10-1000nm. Due to their size the properties get conditioned giving a lager surface area compared to bulk material. Materials made up in such a way will have atoms that have more contact with the external environment; whereas those which are considered as bulk hold the atoms closer to its center [3].

Most commonly used nanoparticles which have biomedical applications are silver, gold, zinc, etc. For this study, an essential mineral Selenium (Se) was used. Se nanoparticles (Nano-Se) are paid much attention in the field of medicine due to their excellent high biological activities and lower toxicities. Selenium Nanoparticles can be used for their effect on the treatment of some human disorders as a nanomedicine. Although recently it is understood that selenium can play a significant role in cancer prevention and possibly therapy [4].

In the present study preparation of selenium nanoparticles (elemental form) was carried out in one step process using chemical method of reduction. A green chemical approach using Ascorbic acid as a reductant is fabricated. Ascorbic Acid is one of the most important vitamins, due to its antioxidant and pH regulator properties; often being added

to various food products and pharmaceuticals. Due to its high water solubility, biodegradability, and low toxicity [5] compared with other chemical reducing agent such as sodium borohydrate ($NaBH_4$).

MATERIALS AND METHODS

Preparation of Se Nanoparticles (Modified Method of Qian Li *et al*)[7]

Na_2SeO_3 and Ascorbic Acid were purchased from Sisco Research Lab pvt ltd, India. A stock of aq. solution of 100mM Sodium selenite and 50mM Ascorbic acid were prepared. Varied sodium selenite to ascorbic acid ratios (1:1, 1:2, 1:3, 1:4, 1:5, 1:6) were reacted from the stock solution. The Ascorbic Acid was added drop wise to the sodium selenite solution under magnetic stirring at different RPM (200, 600, 1000 rpm) at Room Temperature for 30 min. The mixtures were allowed to react with each other in the concentrated form till the color change was observed from colorless to light orange. Soon after the color change was observed the mixture was diluted to 25ml with double distilled water. The as prepared particles were characterized using various analytical tools viz. SEM, Particle size analyzer, Raman spectroscopy, XRD, UV- Vis spectroscopy.

Coating of Se Nanoparticles

Dextrin obtained from maize starch was purchased from Sigma-Aldrich. The selenium nanoparticles prepared earlier were coated with different concentrations of Dextrin (5-20%) using a magnetic stirrer at room temperature using the same procedure as stated above for preparation; instead of adding water; nanoparticles were diluted using solution containing dextrin and the samples were then washed and dried then a pellet was made using KBr. These samples were then analyzed using vacuum FTIR (vertex 80v broker resolution $1cm^{-1}$).

Characterization

The UV-visible spectra of the aqueous samples of different concentrations were recorded in a Perkin Elmer Lambda 25 double beam UV-Vis spectrophotometer from 200 to 800 nm. Particle Size was measured by Nano Particle Size Analyzer (Microtec, Zetatrac NPA 152 Particle Size Analyzer). The Raman spectroscopy and XRD (X-Ray Diffraction) samples were prepared by centrifuging the samples at 12000 rpm for 20 mins at 10°C. The samples were dried at room temperature to get the powder nano selenium. XRD (X-Ray Diffraction) study was done on Bruker Advance 08. The Raman spectroscopy studies were carried out on Renishaw in Via Microscope using Argon lamp at wavelength of 514 nm. The SEM samples were prepared by drying the colloidal suspension on carbon tapes. SEM images were performed using Quanta 200 Scanning Electron Microscope with EDS.

RESULTS AND DISCUSSIONS

In the past, selenium nanoparticles have been prepared using several different methods such as organic acid induced synthesis[8], microwave assisted[9], chemical[10], biological[11]etc.; the reducing agents used for the synthesis are anodic alumina membrane, SDS, mercaptoethanol, sodium borohydrate, glutathione etc. Different shapes of nanoparticles were prepared such as tubes, spheres, wires with a size range of 30 to 200nm[12-14]. The different types of coatings used to stabilize selenium nanoparticles were PVC, Cyclodextrin, CTAB, Betaine hydrochloride, PEG[15-17].

In this study ascorbic acid was used as a reducing agent as it is biocompatible and has good reducing properties forming a spherical nanoparticle having a size range of 20 to 30 nm as measured using particle size analyser. Particles were stabilized by coatig with dextrin. Dextrin is biocompatible and inert. When sodium selenite was allowed to react with

ascorbic acid in ratio of 1:4 the selenium was reduced to elemental selenium (Se^0). The color change from colourless to orange indicated the occurrence of reduction reaction to form selenium nanoparticles.

The mechanisim involved in the formation of nanoparticles (Se^0) was:

$$Aq.\ Na_2SeO_3 \rightarrow 2Na^+ + SeO_3^{2-}\ (pH\ 11) \quad (a)$$

$$Aq.\ C_6H_8O_6 \rightarrow C_6H_7O_6^- + H^+\ (pH\ 2.3) \quad (b)$$

$$2Na^+ + SeO_3^{2-} + C_6H_7O_6^- + H^+ + H_2O \rightarrow Se^0 + 2Na^+ + C_6H_7O_6^- + H_2O\ (pH\ 5.8) \quad (c)$$

Effect of RPM on Maintaining the Nucleation of the Nanoparticle

The reaction was carried out at different rotations per minute (RPM) to check the stirring effect on the reaction rate reducing the polydispersity index and controlling the size of the nanoparticle. Three different ratios of ascorbic acid were reacted with sodium selenite viz 1:3, 1:4 and 1:5 were tested at 200 rpm, 600rpm and 1000rpm. (Figure 1 and Table 1) With increase in RPM there was a decrease polydispersity. Increasing concentration of reductant decreased the size marginally but did not show difference in the polydispersity. Infact using ratio 1:3 and 1000rpm showed decrease in size as well as polydispersity (Figure 1 and Table 1) This concluded that as the rotations per minute increased the particle size decreased reducing the polydispersity index. This further concluded that the RPM played a major role in maintaining the size of the nanoparticles. (As shown in Table 2.)

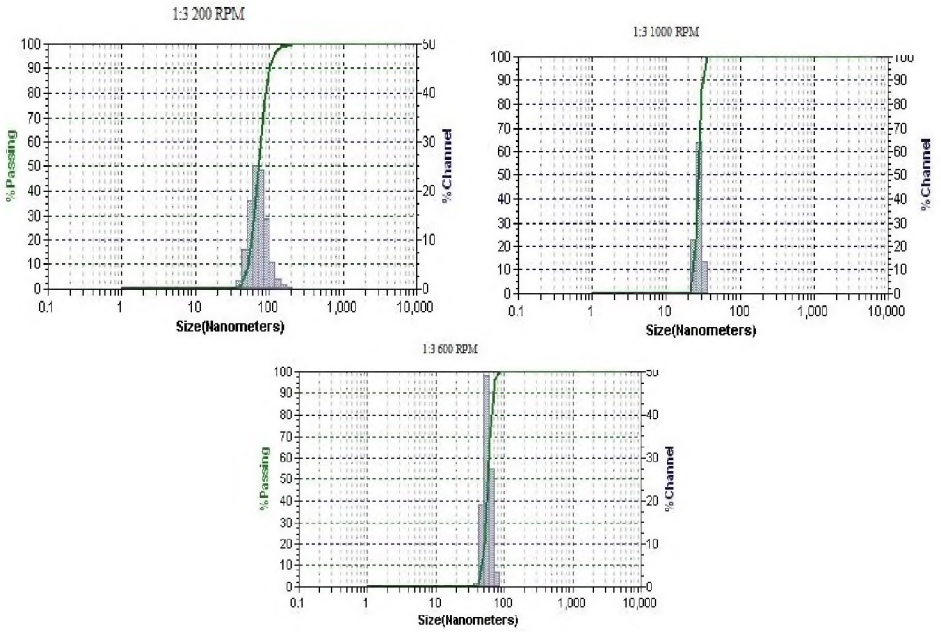

Figure 1: The effect of the RPM was Determined on the Size of the Nanoparticles Using the Concentration Ratios of 1:3, 1:4 and 1:5 and all the Three Samples were Mixed at Different RPM's viz 200rpm, 600rpm and 1000rpm

Table 1: Particle Size of Selenium Nanoparticles Using Different Concentration Ratios at Different 200, 600 and 1000rpm

RPM / Ratio	200	600	1000
1:3	71nm±18nm	56.90nm±7.75nm	27.49nm±2.6nm
1:4	78.1nm±36nm	65.6nm±22.1nm	57.30nm±16.16nm
1:5	92.80nm±20nm	72.5nm±13.4nm	44.8nm±23.39nm

Table 2: Polydispersity Index of Different Concentration Ratios at Different 200, 600 and 1000 rpm

RPM / Ratio	200	600	1000
1:3	0.25	0.136	0.094
1:4	0.46	0.33	0.282
1:5	0.21	0.266	0.522

Characterization of the Se Nanoparticles

All the prepared nanoparticles were scanned from 200nm- 400nm (Fig 2). Strong absorption peak was observed between 320nm to 550nm with maximum at 390nm. The absorption intensity of the spectra increased gradually indicating the amount of reduced Se nanoparticles increased in the solution of different concentrations.

The allotropic form and the purity of the nano Se were further measured by the Raman spectroscopy and SEM-EDS results respectively. The Raman scattering spectra (Fig 3) showed an intensive single resonance peak at 238cm $^{-1}$ which was assigned to the stretching mode of a chain like structure that only exists in the trigonal-Se phase. A small peak at 142cm^{-1} is the transverse optical phonon mode. In addition, the characteristic peak at 256 cm^{-1} and 264cm^{-1} belonging to monoclinic Se and α Se, respectively, did not appear in the Raman spectrum.

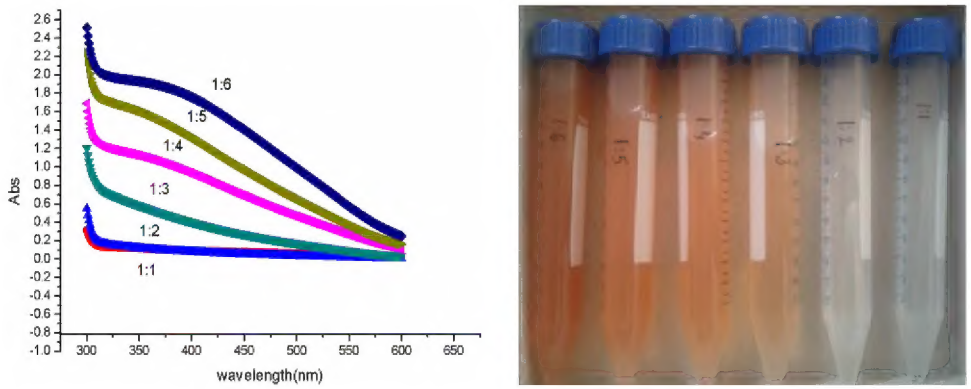

Figure 2: The UV- Visible Spectra of the Different Concentrations. (λ max 390nm)

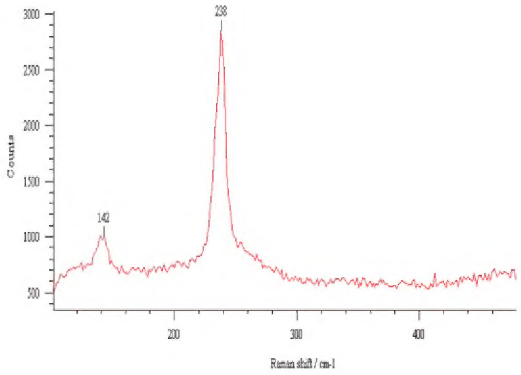

Figure 3: Raman Spectra of Trigonal Se

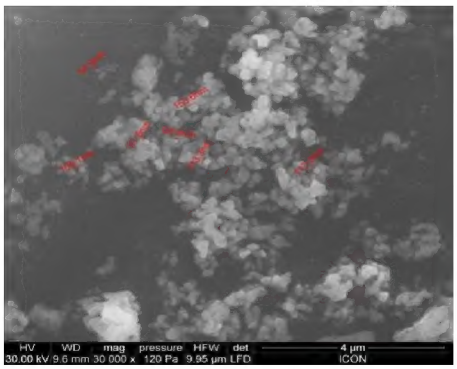

Figure 4: The SEM Analysis of Selenium Nanospheres

Coating of Selenium Nanoparticles

Selenium nanoparticles were coated using Dextrin obtained from Maize starch. The concentrations used for coating selenium nanoparticles varied from 5% - 20%. Further the vacuum FTIR study was carried out to confirm the coating. In dextrin coated nanoparticles, shift in peak1417 cm^{-1} in FTIR spectrum was observed indicating H-C-OH bond. As the concentration of Dextrin increases the shift in the peak from 1417 cm^{-1} to 1384 cm^{-1} was observed which is called as a hypsochromic or a blue shift. The size and PDI of these coated particles were analysed (Table 3). Coating with 10% dextrin showed maximum shift as well as particle size was well controlled at this concentration (Figure 5).

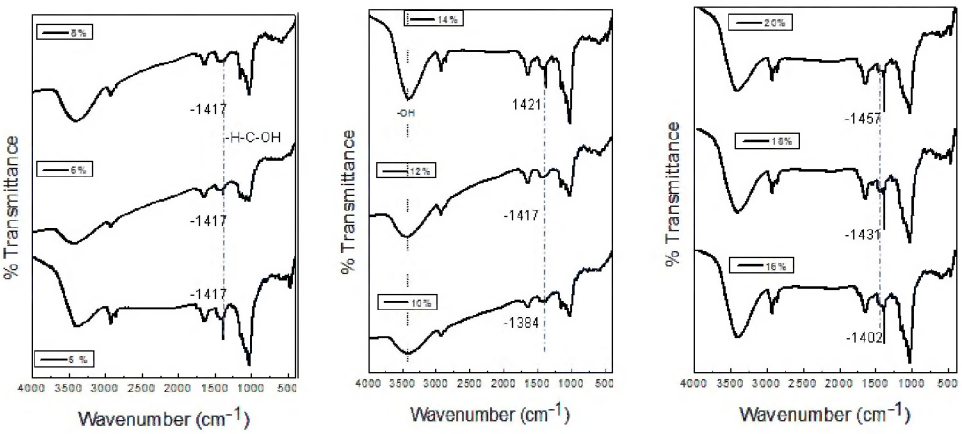

Figure 5: FTIR Spectra of Selenium Nanoparticles Coated with Dextrin (5-20%)

Table 3: Particle Size and Polydispersity Index of the Different Concentration of Dextrin Coated on Selenium Nanoparticles

Dextrin Concentrations (%)	Particle Size (nm)	PDI
6	85.47	0.313
8	74.97	0.177
10	64.40	0.158
12	64	0.185
14	65.50	0.123
16	63.84	0.255
18	62.2	0.126
20	61.95	0.144

CONCLUSIONS

Selenium nanospheres of about 20 – 30 nm were synthesized by the superficial one step method using ascorbic

acid as a reductant which is a biocompatible substance. The zeta potential of selenium nanoaprticles of 1:4 ratio showed – 41.0500mV. Ratios 1:3 and 1:4 were appropriate to be used which also met the needs of the stoichiometric equation. Stirring at Room Temperature for 30 mins at 1000rpm reduced the size as well as polydispersity index. Coating of nanoparticles with 10% Dextrin helped in maintaining the stability and polydispersity of the particles. Dextrin binds on the Selenium nanoparticles at the OH bond in H-C-OH as OSe.

REFERENCES

1. Love Sarin , Vanesa C. Sanchez , Aihui Yan , Agnes B. Kane , and Robert H. Hurt (2010) Selenium-Carbon Bifunctional Nanoparticles for the Treatment of Malignant Mesothelioma. *Adv. Mater.* 22: 5207–5211.
2. Atmir Romero-Perez , Elizabeth Garcia-Garcia , Araceli Zavaleta-Mancera etal (2010) Designing and evaluation of sodium selenite nanoparticles in vitro to improve selenium absorption in ruminants. *Vet Res Commun* 34:71–79.
3. VJ Mohanraj; Y Chen (2006) Nanoparticles – A Review. Tropical *Journal of Pharmaceutical Research India*. 5 (1): 561-573.
4. Atul. R. Ingole Etal (2010) Green Synthesis Of Selenium Nanoparticles Under Ambient Condition *Chalcogenide Letters India* Vol. 7, 485 – 489.
5. Kai Sun, Jingxia Qiu, Jiwei Liu, Yuqing Miao (2009) Preparation and characterization of gold nanoparticles using ascorbic acid as reducing agent in reverse micelles. *J. Matter Sci* 44:754–758.
6. Zhangxu Chen,,Yuhua Shen, Anjian Xie, etal. (2009) L-Cysteine-Assisted Controlled Synthesis of Selenium Nanospheres and Nanorods *Crystal Growth and design*. Vol. 9, No. 3: 1327-1333.
7. Qian Li, Tianfeng Chen, Fang Yang, etal. (2010) Facile and controllable one-step fabrication of selenium nanoparticles assisted by L-cysteine. *Materials Letters* 64: 614–617.
8. Charu Dwivedi, Chetan P. Shah, Krishankant Singh, etal. (2011) An Organic Acid-induced Synthesis and Characterization of Selenium Nanoparticles *Journal of Nanotechnology* 1-6.
9. Hou Ju-ying, AI Shi-yun and SHI Wei-jie (2011) Preparation and Characterization of Nano-Se/Silk Fibroin Colloids chem. *Res. Chinese universities* 27(1), 158—160.
10. Zong-Hong Lin, Fu-Chu Lin and C. R. Chris Wang (2004) Observation in the Growth of Selenium Nanoparticles *Journal of the Chinese Chemical Society* 51, 239-242.
11. Parisa Jafari Fesharaki1, Pardis Nazari1; Mojtaba Shakibaie etal. (2010) Biosynthesis of selenium nanoparticles using klebsiella pneumoniae and their recovery by a simple sterilization process *Brazilian Journal of Microbiology* 41: 461-466.
12. Huiyu Chen, Dong-Wook Shin, Jung-Gyu Nam etal.(2010) Selenium nanowires and nanotubes synthesized via a facile template-free solution method *Materials Research Bulletin* 45: 699–704.
13. Xueyun Gao, Jinsong Zhang, and Lide Zhang (2002) Hollow Sphere Selenium Nanoparticles: Their In-Vitro Anti Hydroxyl Radical Effect Adv. Mater. 14, No. 4.

14. Sanjeev Kumar (2011) Synthesis and characterisation of selenium nanowires using template synthesis *Journal of Experimental Nanoscience* Vol. 4, No. 4, 341–346.

15. Joseph F Ramos, Thomas J Webster (2012) Cytotoxicity of selenium nanoparticles in rat dermal fibroblasts *International Journal of Nanomedicine* vol no. 7 3907–3914.

16. Haibing li and Cuiping Han (2008) sonochemical synthesis of cyclodextrin coated quantum dots for optical detection of pollutant phenols In water *Chem. Mater* 20 (19), 6053–6059.

17. Shanyuan Zheng, Xiaoling Li, Yibo Zhang (2012) PEG-nanolized ultrasmall selenium nanoparticles overcome drug resistance in hepatocellular carcinoma HepG2 cells through induction of mitochondria dysfunction *International Journal of Nanomedicine* vol no. 7 3939–3949.NYSTAL GROWTH